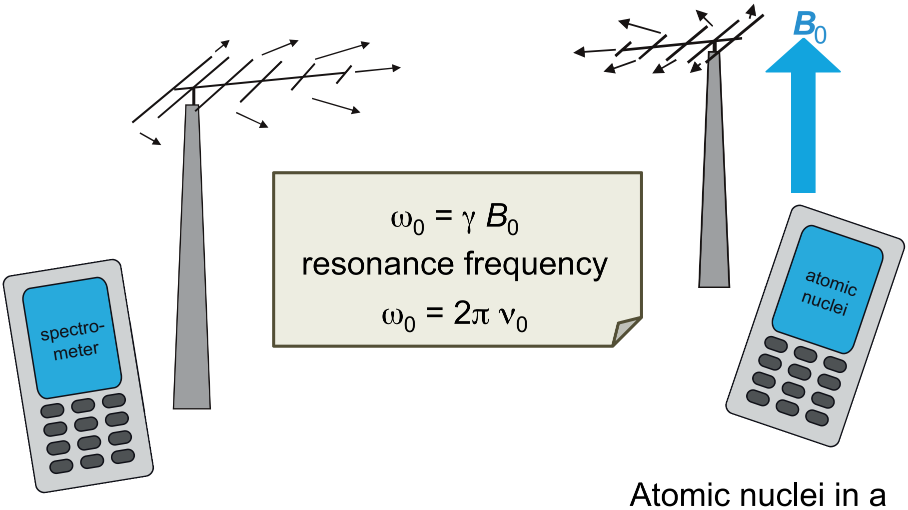
2. Basic Principles

NMR spectrum
Nuclear magnetism
Rotating coordinate frame
NMR spectrometer
Pulsed NMR
Fourier transformation
Phase correction
Relaxation
Spin echo
Measurement methods
Spatial resolution
Fourier and Laplace NMR

B. Blümich, *Essential NMR*,
https://doi.org/10.1007/978-3-030-10704-8_2

NMR is a Form of Telecommunication in a Magnetic Field



$\omega_0 = \gamma B_0$

resonance frequency

$\omega_0 = 2\pi \nu_0$

NMR spectrometer

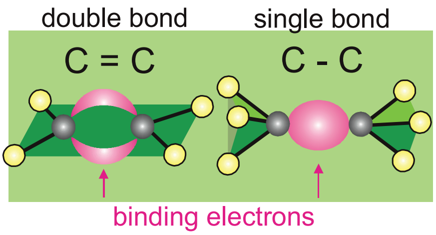
Atomic nuclei in a magnetic field $\boldsymbol{B}_0$

Properties of Atomic Nuclei

- Some magnetic isotopes important to NMR are listed below along with their resonance frequencies ν_0 at 1 T field strength, natural abundance, and sensitivity relative to ^{13}C
- Chemical shift range and reference compound are relevant for chemical analysis by NMR spectroscopy
- ^{1}H is the most sensitive stable nucleus for NMR and the most abundant nucleus in the universe

Nuclear isotope	Natural abundance [%]	Sensitivity rel. to ^{13}C	Spin	ν_0 at 1.0 T [MHz]	Chemical shift range [ppm]	Reference compound
^{1}H	99.99	5878	½	42.58	12 to −1	$SiMe_4$
^{2}H	0.01	0.00652	1	6.54	12 to −1	$SiMe_4$
^{13}C	1.07	1.0	½	10.71	240 to −10	$SiMe_4$
^{15}N	0.36	0.0223	½	30.42	1200 to −500	$MeNO_2$
^{19}F	100.00	4890	½	40.06	100 to −300	$CFCl_3$
^{29}Si	4.69	2.16	½	8.46	100 to −400	$SiMe_4$
^{31}P	100.00	391	½	17.24	230 to −200	H_3PO_4

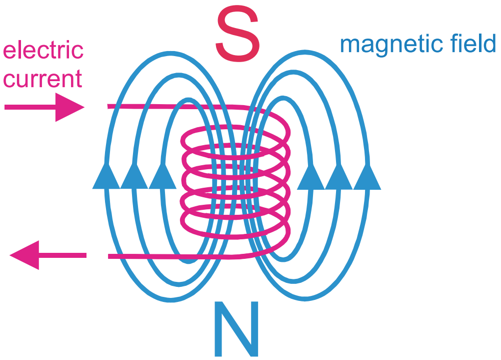
Electrons in Motion



Distributions of binding electrons

Moving charges generate a magnetic field

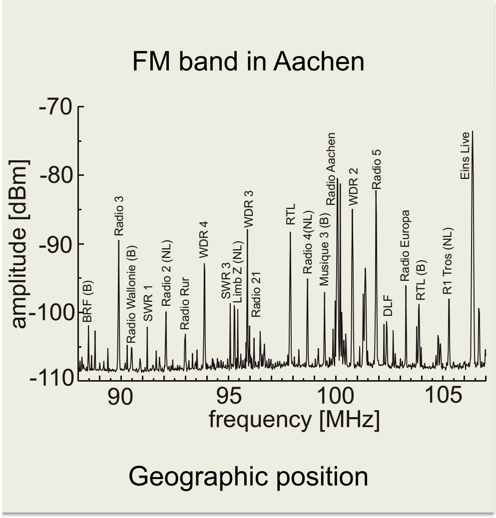
Example: coil



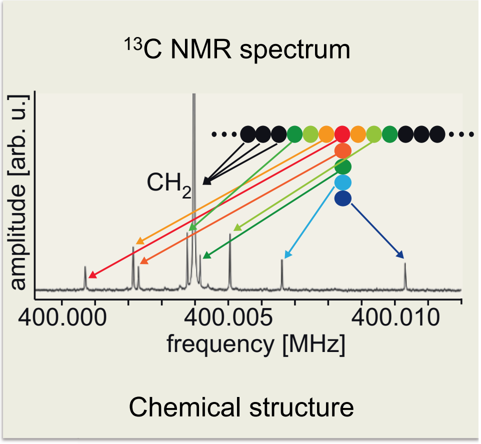
Magnetic Shielding

- The NMR frequency is determined by the magnetic field at the site of the nucleus
- Atomic nuclei are surrounded by electrons
- In molecules, the electrons of the chemical bond are shared by different nuclei
- Electrons of atoms and molecules move in orbitals, which are studied in quantum mechanics
- The orbitals of the binding electrons are characteristic of the *chemical structure* of the molecule
- Electrons carry an electric charge
- Electric charges in motion generate a magnetic field
- The internal magnetic field generated by the electrons moving in the external magnetic field $\boldsymbol{B}_0$ is usually opposed to $\boldsymbol{B}_0$. It shields the nucleus from $\boldsymbol{B}_0$

Frequency Distributions of Radio Waves


FM band in Aachen

Geographic position


^{13}C NMR spectrum

Chemical structure

Spectra are fingerprints

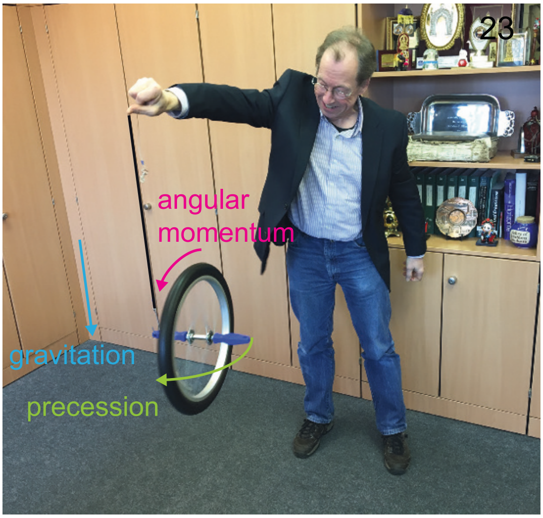
Chemical Shift

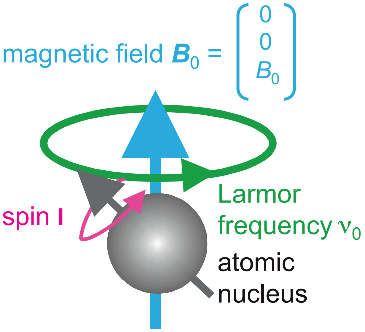
- The magnetic field generated by the electrons shifts the resonance frequency,

$$\omega_0 = 2\pi\,\nu_0 = \gamma\,(1 - \sigma)\,B_0$$

- The quantity σ is the *magnetic shielding* for a given chemical group
- The quantity $\delta = (\nu_0 - \nu_{\mathrm{ref}}) / \nu_{\mathrm{ref}}$ is the *chemical shift* of a chemical group. It is independent of the strength B_0 of the magnetic field
- The quantity ν_{ref} is the reference frequency, for example, the resonance frequency of tetramethyl silane (TMS: SiMe_4) for ^{1}H and ^{13}C NMR
- The chemical shift can be calculated from tabulated chemical shift increments as well as *ab initio* from quantum mechanics
- Magnetically inequivalent chemical groups possess different chemical shifts
- In liquids narrow resonance signals are observed with typical widths of 0.1 Hz
- The distribution of resonance frequencies forms the *NMR spectrum*
- The NMR spectrum is an easy-to-read fingerprint of the molecular structure in a way similar to the distribution of FM radio signals at a given location, which provides a fingerprint of the geographic position
- NMR spectra of molecules in solution are measured routinely for chemical identification and structural analysis

Spin and Precession





Arnold Sommerfeld, 1868 – 1951. Heisenberg's teacher: Theory of the spinning top (Wikimedia, public domain)

Paul Adrien Maurice Dirac, 1902 – 1984. Nobel prize in Physics 1933: Theory of the spin (Wikimedia, public domain)

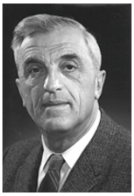
Otto Stern 1888 – 1963. Nobel prize in Physics 1943: Experimental proof of the spin (Wikimedia, public domain)

Nuclear Magnetism

- In an NMR sample of material there are of the order of 1 mole or 6×10^{23} atomic nuclei
- 1 mole is 18 g of water. It would take a human 20,000 times the age of the universe to count to one mole
- Some atomic nuclei appear to spin and exhibit an angular momentum
- Examples: ^{1}H, ^{2}H, ^{13}C, ^{15}N, ^{19}F, ^{29}SI, ^{31}P
- Because atomic nuclei are small elementary particles, the laws of classical physics do not apply. Instead the laws of *quantum mechanics* do
- In the laws of physics involving elementary particles *Planck`s constant* $h = 2\pi\hbar$ appears
- According to quantum mechanics an elementary particle with an *angular momentum* $\hbar \boldsymbol{I}$ or *spin* $\boldsymbol{I}$ also possesses a magnetic dipole moment $\mu = \gamma \hbar \boldsymbol{I}$
- A classical object with angular momentum is the spinning *bicycle wheel*
- A wheel spinning in a gravitational field formally follows the same laws as a spin in a magnetic field: it precesses around the direction of the field
- In NMR the *precession frequency* is called the *Larmor frequency*

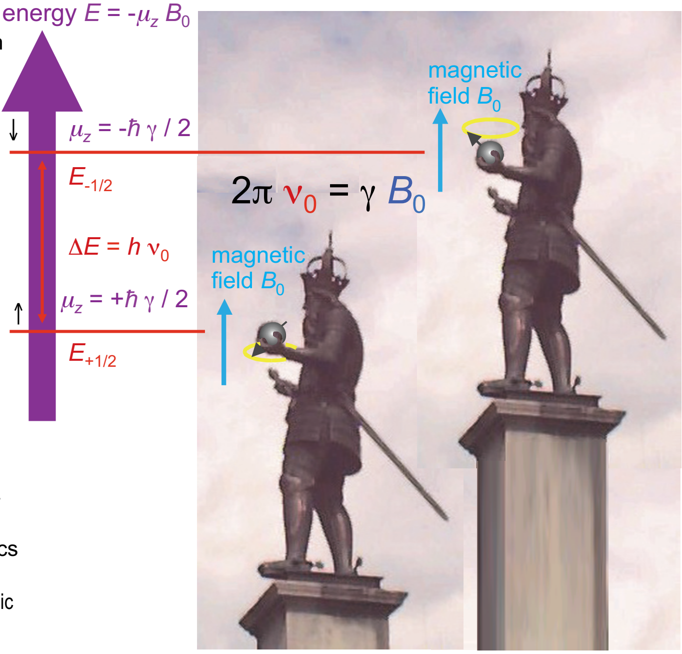
Quantum Mechanics

Niels Henrik David Bohr, 1885 – 1962. Nobel prize in Physics 1922: $\Delta E = h\,\nu$ (Wikimedia, public domain)



Felix Bloch, 1905 – 1983. Nobel prize in Physics 1952: NMR. Scholar of Heisenberg (Wikimedia, CC BY-SA 3.0)

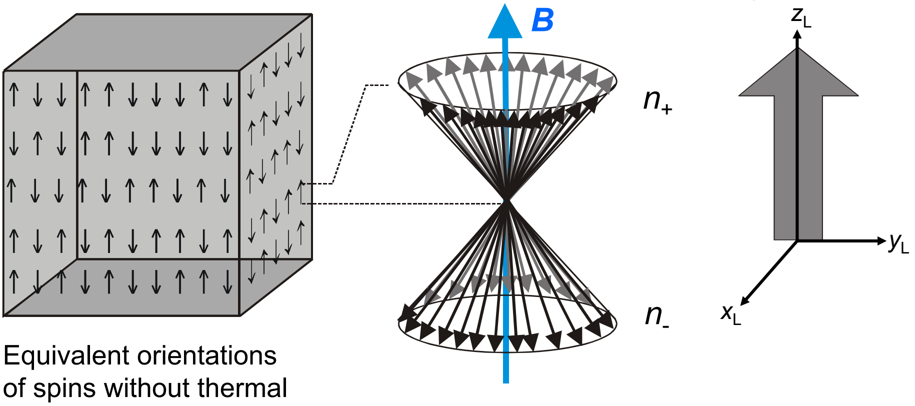
Edward Mills Purcell1912 – 1997. Nobel prize in Physics 1952: NMR (Wikimedia, public domain)



Properties of Nuclear Spins

- Following Heisenberg's uncertainty principle, only the component of the spin in the direction of the magnetic field can be determined accurately
- From quantum mechanics it is known that a spin with the *spin quantum number I* can assume $2I + 1$ stable orientations in a magnetic field
- The projection of the spin angular momentum along the direction of the magnetic field is proportional to the *magnetic quantum number m*, where $m = I, I-1, \ldots, -I$
- $I = ½$ applies to the nuclei ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P, and $I = 1$ to ^{2}H, ^{14}N
- For nuclei with spin $I = ½$ there are two possible orientations of it's projection along the axis of the magnetic field: ↑ ($m = +1/2$) and ↓ ($m = -1/2$)
- Both orientations differ in the interaction energy $E_m = -\hbar\,\gamma\,m\,B_0$ of the nuclear magnetic dipoles with the magnetic field $\boldsymbol{B}_0$
- According to Bohr's formula $\Delta E = h\,\nu_0$ the energy difference $\Delta E = E_{-1/2} - E_{+1/2} = \hbar\,\gamma\,B_0$ associated with both orientations corresponds to the frequency $\omega_0 = 2\pi\,\nu_0 = \gamma\,B_0$
- Here ν_0 is the precession frequency of the nuclear spins in the magnetic field

Macroscopic Magnetization



Macroscopic sample:
10^{23} nuclear spins

$n_-/n_+ = \exp\{-\Delta E/k_B T\}$

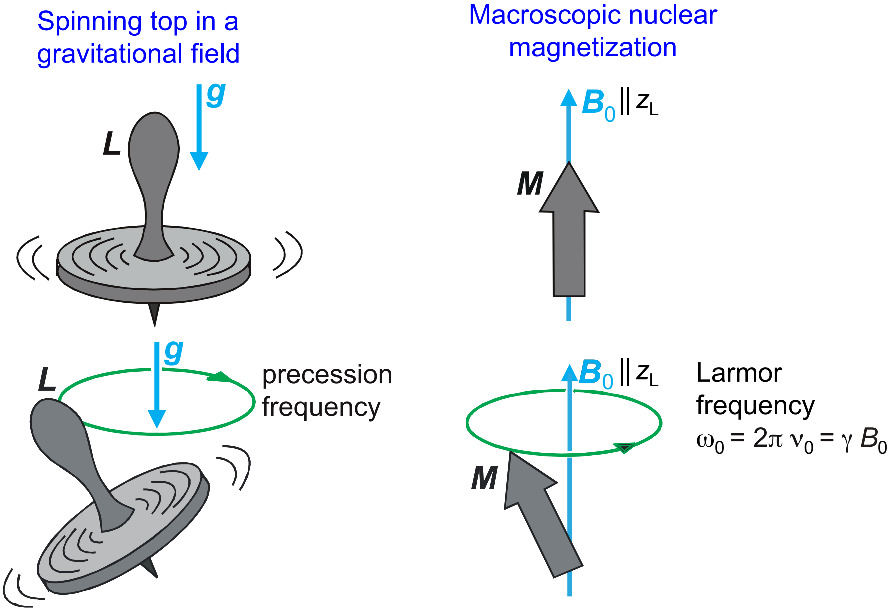
Vector sum:
macroscopic
magnetization ***M***

Equivalent orientations
of spins without thermal
motion

Nuclear Magnetization in Thermodynamic Equilibrium

- At room temperature, all magnetic dipole moments change their orientations in the magnetic field rapidly, because the thermal energy $k_B T$ is orders of magnitude larger than the energy difference $\Delta E = h \nu_0$ between spin states
- The average orientation of all spins in thermal motion is commonly mapped onto the orientations of cold spins not agitated by temperature and aligned either parallel or anti-parallel to the direction of the magnetic field
- All (classical) magnetic dipole moments add as vectors. Their components in each space direction are additive
- The sum of transverse components vanishes
- The sum of longitudinal components forms the *longitudinal magnetization*
- This component is referred to as the *magnetic polarization* of the nuclei or the *nuclear magnetization*
- At room temperature only about 10^{18} spins of 10^{23} spins contribute the macroscopic nuclear magnetization of the sample
- In thermodynamic equilibrium, the nuclear magnetization is oriented parallel to the direction of the magnetic field
- By convention the direction of the magnetic field defines the z direction of the *laboratory coordinate frame* LCF with coordinates x_L, y_L, z_L

Precession of Nuclear Magnetization



Bloch's Equation

- When the magnetization ***M*** is not aligned with the field direction z_L, it precesses around z_L with the frequency ν_0 in analogy with the precession of a top spinning with angular momentum ***L*** exposed to a gravitational force $m\boldsymbol{g}$
- The precession is described by the equation for the magnetic *spinning top*:

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{M} = \gamma\, \boldsymbol{M} \times \boldsymbol{B}$$

- This equation states that any change d***M*** of the magnetization ***M*** is perpendicular to ***M*** and ***B***; therefore ***M*** precesses around ***B***
- In general any macroscopic precessional motion is attenuated. This is why Felix Bloch introduced phenomenological attenuation terms:

$$\mathbf{R} = \begin{pmatrix} 1/T_2 & 0 & 0 \\ 0 & 1/T_2 & 0 \\ 0 & 0 & 1/T_1 \end{pmatrix}$$

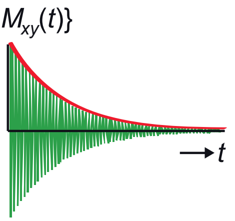
- The resultant equation is the *Bloch equation*,

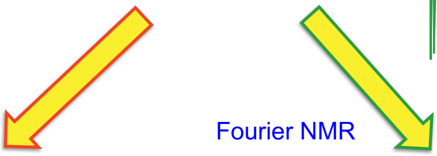
$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{M} = \gamma\, \boldsymbol{M} \times \boldsymbol{B} - \mathbf{R}\,(\boldsymbol{M} - \boldsymbol{M}_0),$$

  where $\boldsymbol{M}_0$: initial magnetization, T_1: *longitudinal relaxation time*, and T_2: *transverse relaxation time*, ***B***: any magnetic field
- Note: The Bloch equation formulates a left-handed *rotation* of the *transverse magnetization*. But for convenience sake a right-handed one is used in the illustrations in this book and much of the literature

Transverse Magnetization

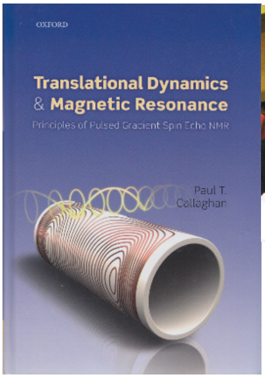
$$M_{xy}(t) = M_{xy}(0)\,\exp\{-(1/T_2 + i\,\omega_0)\,t\}$$





Laplace NMR

Fourier NMR



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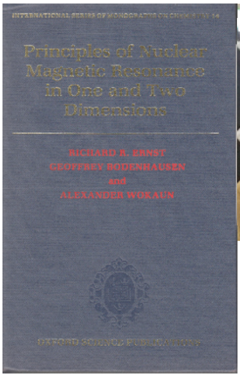
Principles of Pulsed Gradient Spin Echo NMR

Paul T. Callaghan

2011

The legacy of Paul Callaghan



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Principles of Nuclear Magnetic Resonance in One and Two Dimensions

RICHARD R. ERNST
GEOFFREY BODENHAUSEN
and
ALEXANDER WOKAUN

OXFORD SCIENCE PUBLICATIONS

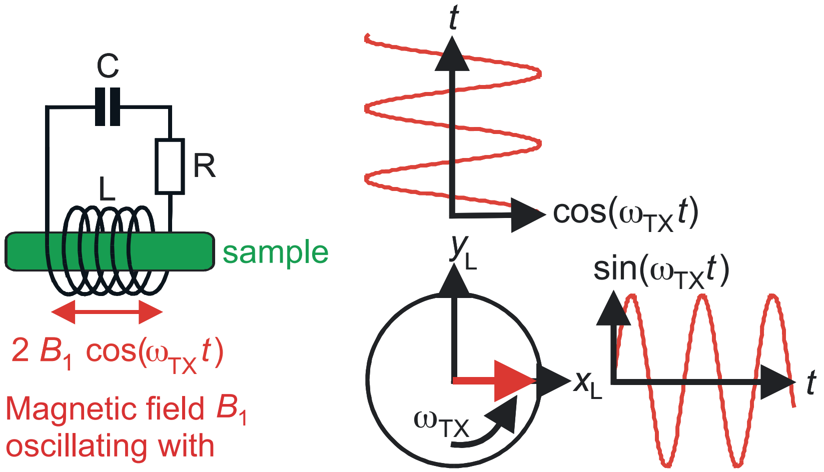
1987

The legacy of Richard Ernst

Transverse Magnetization

- Bloch's equation can be solved when spelling it out for the magnetization components with the *thermodynamic equilibrium magnetization* M_0,
  $\mathrm{d}M_{xL}/\mathrm{d}t = \gamma\,(M_{yL}\,B_{zL} - M_{zL}\,B_{yL}) - M_{xL}/T_2$
  $\mathrm{d}M_{yL}/\mathrm{d}t = \gamma\,(M_{zL}\,B_{xL} - M_{xL}\,B_{zL}) - M_{yL}/T_2$
  $\mathrm{d}M_{zL}/\mathrm{d}t = \gamma\,(M_{xL}\,B_{yL} - M_{yL}\,B_{xL}) - (M_{zL} - M_0)/T_1$
- In the laboratory coordinate frame, the magnetic field vector is
  $\boldsymbol{B} = (B_{xL}, B_{yL}, B_{zL})^\dagger = (2B_1\cos\omega_{TX}t, 0, B_0)^\dagger$,
  where ω_{TX} is the transmitter frequency
- Writing the transverse magnetization in complex form as $M_{xy} = M_{xL} + iM_{yL}$, for $B_1 = 0$ the evolution of the transverse magnetization follows the equation
  $\mathrm{d}M_{xy}/\mathrm{d}t = -\,i\,\gamma\,M_{xy}\,B_0 - M_{xy}/T_2$
- With $\omega_0 = \gamma\,B_0$, the solution provides the *free induction decay* (*FID*) in the laboratory frame, describing an attenuated left-handed *rotation*,
  $M_{xy}(t) = M_{xy}(0)\,\exp\{-(1/T_2 + i\,\omega_0)t\} = M_{xy}(0)\,\exp\{-t/T_2\}\,\exp\{-i\,\omega_0 t\}$
- This FID can be generated with an rf excitation impulse. Therefore it is also known as the NMR impulse response
- The FID is the product of a decaying and an oscillating exponential function
- In real matter many decay rates $1/T_2$ and oscillation frequencies ω_0 arise
- *Distributions of frequencies* are retrieved from $M_{xy}(t)$ by *Fourier transformation*. *Distributions of relaxation rates* are retrieved from $|M_{xy}(t)|$ by algorithms reminiscent of the *inverse Laplace transformation*

Magnetic Fields in an Oscillator Circuit



$2\,B_1 \cos(\omega_{TX} t)$

Magnetic field B_1 oscillating with frequency ω_{TX}

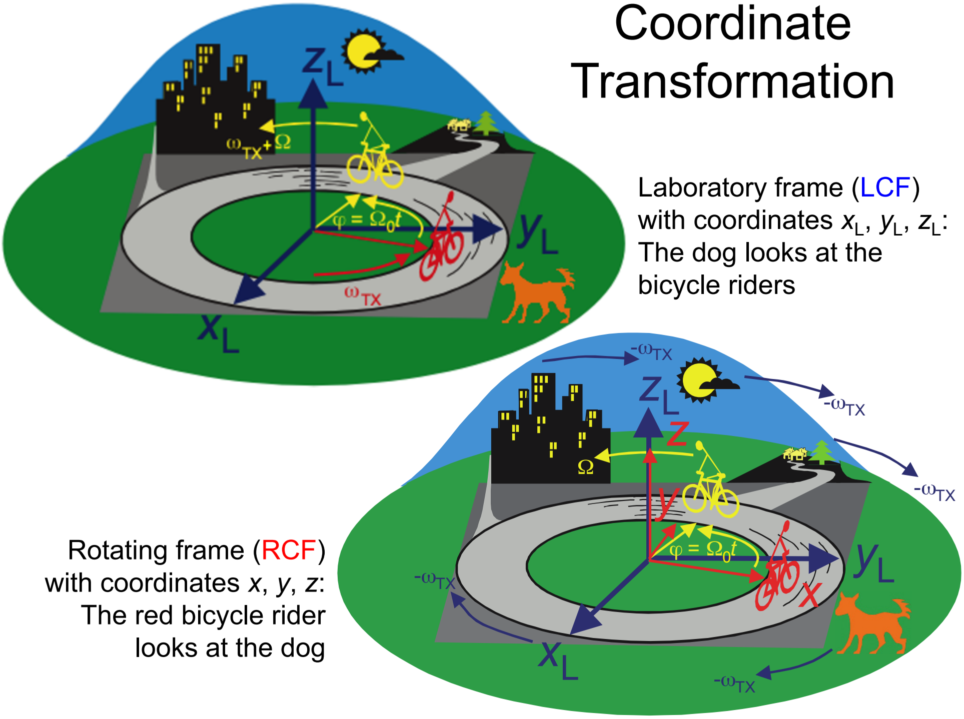
$$\exp\{i\omega_{TX} t\} = \cos(\omega_{TX} t) + i \sin(\omega_{TX} t)$$

$$2\;B_1 \cos(\omega_{TX} t) = B_1 [\exp\{i\omega_{TX} t\} + \exp\{-i\omega_{TX} t\}]$$

Contacting Nuclear Magnetization

- Nuclear magnetization can be rotated away from the direction z_L of the magnetic field $\boldsymbol{B}_0$, which keeps the spins aligned, by a magnetic field $\boldsymbol{B}_1$ perpendicular to $\boldsymbol{B}_0$ oscillating in resonance with the precession frequency
- This field $\boldsymbol{B}_1$ oscillates in the *radio-frequency* (rf) regime with frequency ω_{TX} and is generated by a *transmitter* TX
- For maximum interaction of the rotating field with the nuclear magnetization both frequencies need to match, defining the *resonance condition* $\omega_{TX} = \omega_0$
- Radio-frequency electromagnetic waves are produced by currents oscillating in electronic circuits and are emitted from transmission antennas
- An *electric oscillator* consists of a *coil* with inductance L, a capacitor with capacitance C, and a resistor with resistance R
- The coil generates a linearly polarized, oscillating magnetic field $2B_1 \cos(\omega_{TX} t)$
- Two orthogonal, linearly polarized waves $\cos(\omega_{TX} t)$ and $\sin(\omega_{TX} t)$ generate a rotating wave
- The linearly polarized wave $2 \cos(\omega_{TX} t)$ of the coil can be decomposed into a right rotating wave $\exp\{i\omega_{TX} t\}$ and a left rotating wave $\exp\{-i\omega_{TX} t\}$, one of which can be adjusted to resonate with the precessing magnetization
- For optimum use of the oscillating magnetic field, the sample to be investigated is placed inside the coil of the electronic oscillator

Coordinate Transformation



Laboratory frame (LCF) with coordinates x_L, y_L, z_L: The dog looks at the bicycle riders

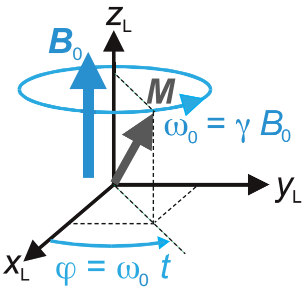
Rotating frame (RCF) with coordinates x, y, z: The red bicycle rider looks at the dog

Rotating Coordinate Frame

- Transformations from one coordinate frame into another change the point of view, i. e. they change the mathematics but not the physics
- As the precession of nuclear magnetization is a rotational motion and the rf excitation is a rotating wave, the magnetization is conveniently studied in a *rotating coordinate frame* (RCF) with coordinates x, y, z
- The dog at the traffic circle is positioned in the *laboratory coordinate frame* (LCF) with coordinates x_L, y_L, z_L: For the dog the bicycles are moving in the traffic circle with angular velocities ω_{TX} and $\omega_{TX}+\Omega_0$
- The cyclists on the bicycles are viewing the world from the RCF. They are at rest in their respective RCFs
- For the red cyclist the world in the LCF is rotating against the direction of his bicycle with angular velocity $-\omega_{TX}$
- For the red cyclist the yellow bicycle moves away with angular velocity Ω_0
- The connecting vectors from the center of the traffic circle to the bicycles correspond to the magnetization vectors in the transverse *xy* plane
- The angular velocity of the RCF as seen in the LCF corresponds to the frequency ω_{TX} of the rf wave
- The spectrometer hardware assures that the NMR signal is measured in the RCF

Action of rf Pulses

Laboratory coordinate frame (LCF)

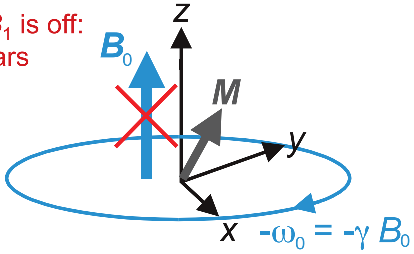


M precesses around $\boldsymbol{B}_0$

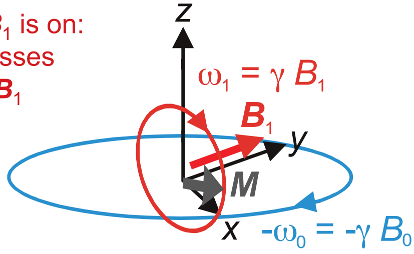
90° pulse: $\omega_1 t_p = \pi/2$
180° pulse: $\omega_1 t_p = \pi$

Rotating coordinate frame (RCF)

rf field $\boldsymbol{B}_1$ is off: ***M*** appears static



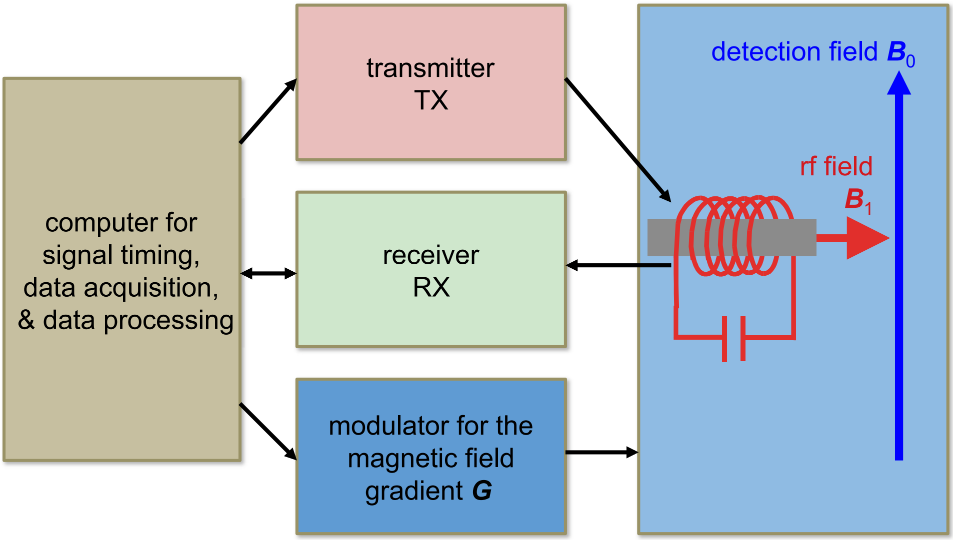
rf field $\boldsymbol{B}_1$ is on: ***M*** precesses around $\boldsymbol{B}_1$



Radio-Frequency Pulses

- Radio-frequency (rf) pulses produce a magnetic field $\boldsymbol{B}_1$, which oscillates with frequency ω_{TX}
- In the rotating coordinate frame RCF, which rotates on resonance with the precession frequency $\omega_{TX} = \omega_0 = \gamma B_0$ around the z_L axis, the magnetization ***M*** appears at rest even if it is not parallel to the magnetic field $\boldsymbol{B}_0$
- When the magnetization is not rotating, there is no torque on the magnetization, so that in the RCF rotating on resonance with $\omega_{TX} = \omega_0$ the magnetic field $\boldsymbol{B}_0$ vanishes
- When the transmitter generates a $\boldsymbol{B}_1$ field rotating at the frequency ω_{TX} of the RCF in the LCF, this field appears static in the RCF
- In the RCF the magnetization rotates around the $\boldsymbol{B}_1$ field with frequency $\omega_1 = \gamma B_1$ in analogy to the *rotation* with frequency $\omega_0 = \gamma B_0$ around the $\boldsymbol{B}_0$ field in the LCF
- If B_1 is turned on in a pulsed fashion for a time t_p, a 90° pulse is defined for $\omega_1 t_p = \pi/2$ and a 180° pulse for $\omega_1 t_p = \pi$
- The phase φ_{TX} of the *rotating rf field* $B_1\exp\{i\omega_{TX}t + i\,\varphi_{TX}\}$ defines the direction of the B_1 field in the *xy* plane of the RCF
- Using this phase the magnetization can be rotated in the RCF around different axes, e. g. $90°_y$ denotes a positive 90° *rotation* around the *y* axis of the RCF and $180°_x$ a positive 180° rotation around the *x* axis

Spectrometer Hardware



computer for signal timing, data acquisition, & data processing

transmitter TX

receiver RX

modulator for the magnetic field gradient ***G***

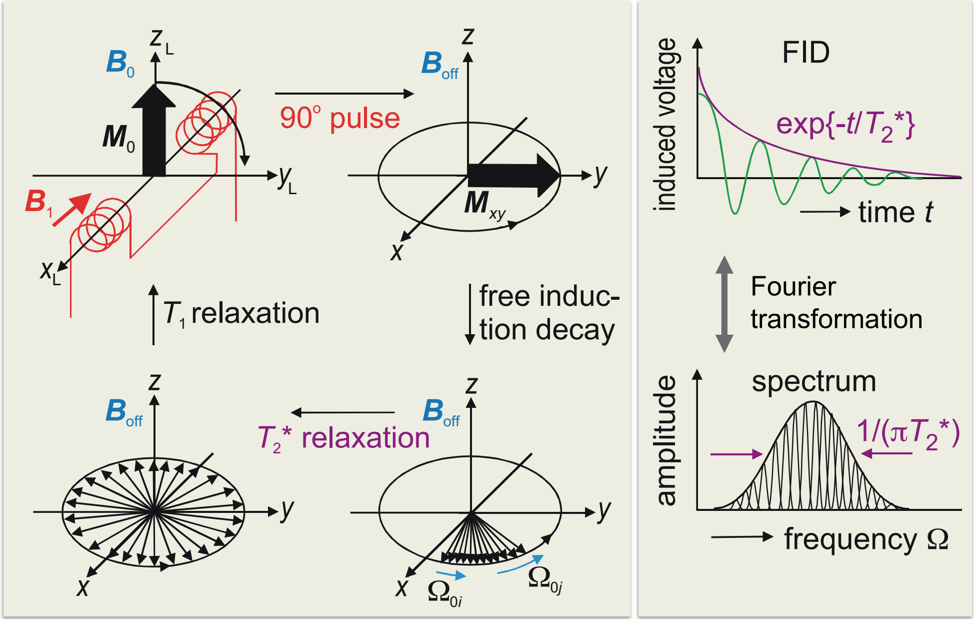
detection field $\boldsymbol{B}_0$

rf field $\boldsymbol{B}_1$

NMR Spectrometer

- The sample is positioned in a magnetic field $\boldsymbol{B}_0$ inside or next to an rf coil, which is part of an rf *oscillator* tuned to the frequency ω_{TX}
- The oscillator is connected under computer control either to the rf *transmitter* (TX) or to the *receiver* (RX)
- A 90° rf pulse from the transmitter rotates the magnetization from the z_L direction of the $\boldsymbol{B}_0$ field into the transverse plane
- Following the pulse, the transverse magnetization components precess around the z_L axis of the LCF with frequency ω_0
- According to the dynamo principle, the precessing magnetization induces a voltage in the coil, which oscillates at frequency ω_0
- In the receiver, this signal is mixed with a reference wave at frequency ω_{TX}, and the audio signal at the difference frequency is acquired for further analysis
- This step is the transition into the *rotating coordinate frame*
- Depending on the phase $\varphi_{RX} = 0°$ and $90°$ of the reference wave $\cos(\omega_{TX}t+\varphi_{RX})$ the *components* $\cos(\omega_0-\omega_{TX})t$ and $\sin(\omega_0-\omega_{TX})t$ of the transverse magnetization are measured in the RCF at frequency $\Omega_0 = \omega_0 - \omega_{TX}$
- Usually the in-phase and the *quadrature component* are measured together
- For imaging and flow measurements the spectrometer is equipped with switchable *gradient fields* in x_L, y_L, and z_L directions of the LCF

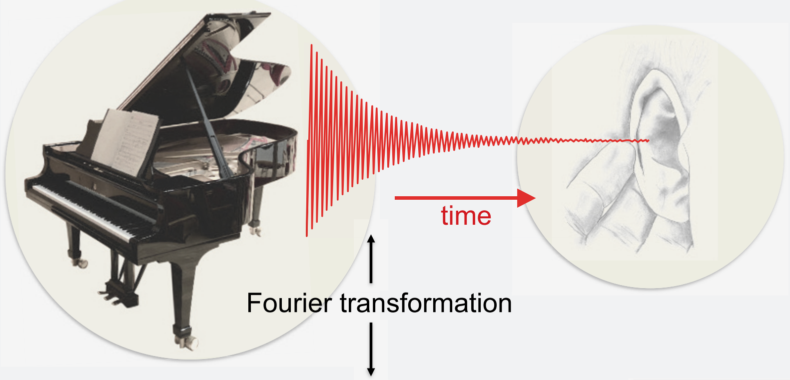
Fourier NMR



Pulsed Excitation

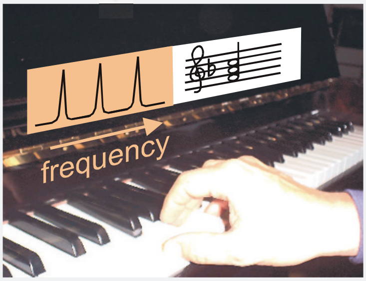
- Outside a magnetic field the magnetic dipole moments of the nuclear spins are oriented in random directions in space
- In a magnetic field $\boldsymbol{B}_0$, the nuclear spins partially align with the field and form the *longitudinal magnetization* $\boldsymbol{M}_0$ parallel to $\boldsymbol{B}_0$ in a characteristic time T_1 following the rate equation $M_z(t) = M_0\,(1 - \exp\{-t/T_1\})$
- T_1 is the *longitudinal relaxation time*
- A resonant 90° rf pulse from the transmitter rotates the magnetization from the z direction of the magnetic field $\boldsymbol{B}_0$ into the transverse plane of the RCF
- After the pulse the transverse magnetization components $M_{xy,i}$ precess around the z axis of the RCF with the difference frequencies $\Omega_{0i} = \omega_{0i} - \omega_{TX}$
- Each component $M_{xy,i}$ corresponds to a different chemical shift or another position in the sample with a different magnetic field at the site of the nuclei
- The vector sum of the *transverse magnetization* components decays with the time constant T_2^* due to destructive interference of the components with different precession frequencies Ω_{0i}
- T_2^* is the apparent *transverse relaxation time.* It is determined by time-invariant and time-dependent local magnetic fields at the sites of the spins
- The signal-decay envelope is often exponential: $M_{xy}(t) = M_z(0)\exp\{-t/T_2^*\}$
- The signal induced in the coil after an excitation pulse is the FID
- For one component it is $M_{xy}(t) = M_z(0)\exp\{-(1/T_2^* + i\Omega_0)t\}$ after a 90° pulse
- A frequency analysis of the FID by *Fourier transformation* produces the *NMR spectrum* with a *linewidth* $\Delta\Omega = 1/(\pi T_2^*)$

Frequency Analysis



Jean Baptiste
Joseph Fourier
1768 - 1830
(http://web.mit.edu/2.51/www/fourier.jpg: public domain)

Fourier transformation



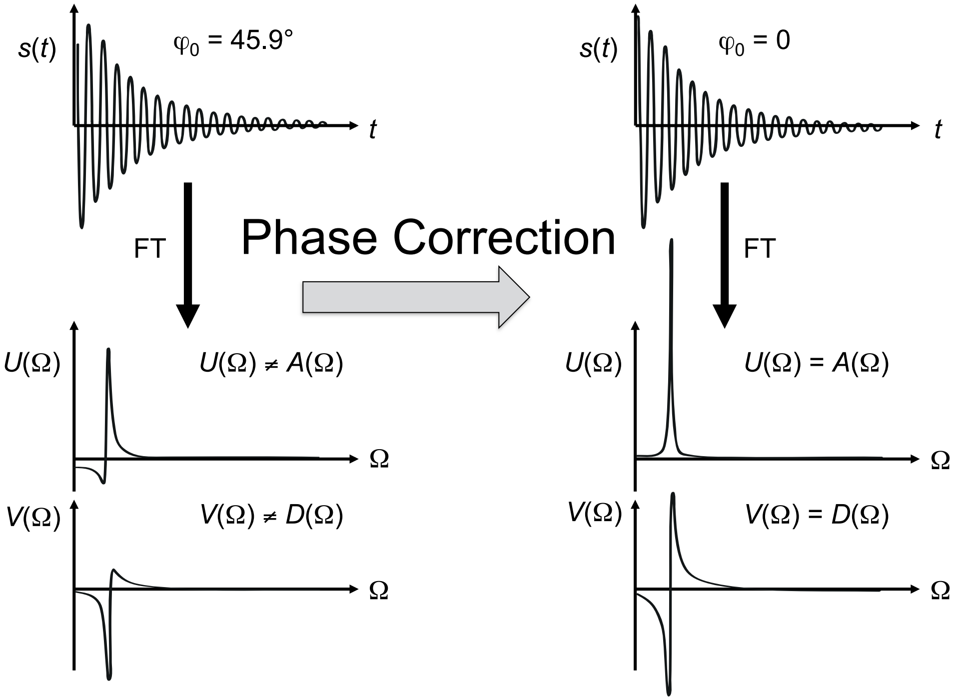
Free induction decay (FID):
Time *t*

Fourier transformation

Spectrum: Frequency Ω

Fourier Transformation

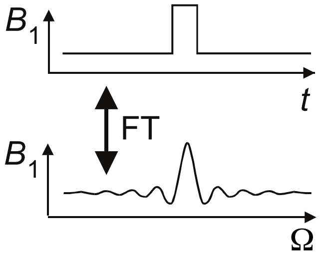
- J.B.J. Fourier introduced the transformation named after him when studying thermal conductivity
- The *Fourier transformation* (FT) is a decomposition of a function $s(t)$ into harmonic waves $\exp\{\mathrm{i}\,\Omega t\} = \cos(\Omega t) + \mathrm{i}\sin(\Omega t)$ with variable frequency Ω
- In NMR the *FID* $s(t)$ is transformed to the spectrum $S(\Omega)$ of cosine and sine waves: $S(\Omega) = \int s(t)\exp\{+\mathrm{i}\Omega t\}\,\mathrm{d}t$
- The *spectrum* $S(\Omega) = U(\Omega) + \mathrm{i}\,V(\Omega)$ consists of a real part $U(\Omega)$ and an imaginary part $V(\Omega)$
- Often only the magnitude spectrum $|S(\Omega)| = [U(\Omega)^2 + V(\Omega)^2]^{1/2}$ is considered
- The Fourier transformation corresponds to the transformation of an acoustic signal into the pitch and volume of sound
- For the discrete Fourier transformation there is a fast algorithm, which was rediscovered in 1965 by J. W. Cooley and J. W. Tukey
- The algorithm requires discrete representations of time $t = n\,\Delta t$ and frequency $\Omega = n\,\Delta\Omega$ at intervals Δt and $\Delta\Omega$, whereby range and step size are related via the acquisition time $n_{\max}\,\Delta t$ of the NMR signal following $\Delta\Omega = 1/(n_{\max}\,\Delta t)$
- The abscissa of the discrete spectrum corresponds to the keys of a piano
- The spectral amplitude corresponds to the volume of a given tone
- NMR spectroscopy and imaging with pulsed excitation rely on the Fourier transformation for data processing. They are referred to as *Fourier NMR*
- The product of two Fourier conjugated variables, e.g. t and Ω, is always an angle. It is referred to as *phase* φ



Signal Processing

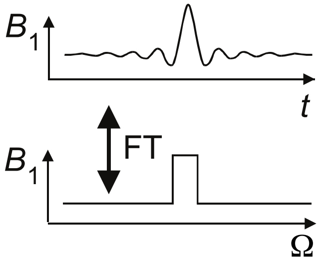
- Depending on the electronics of the receiver, the NMR signal $s(t) = s(0)\exp\{-[1/T_2 + i\Omega_0]\, t + i\,\varphi_0\}$ of a magnetization component is recorded in practice with a phase offset φ_0
- For $\varphi_0 = 0$ the real part $U(\Omega)$ of the *Fourier transform* $S(\Omega)$ is an *absorption signal* $A(\Omega)$ and the imaginary part $V(\Omega)$ a *dispersion signal* $D(\Omega)$
- For $\varphi_0 \neq 0$ the real and imaginary components of $S(\Omega)$ are mixed in $U(\Omega)$ and $V(\Omega)$, and the associated complex *spectrum* $S(\Omega) = U(\Omega) + i\,V(\Omega) = [A(\Omega) + i\,D(\Omega)]\exp\{i\,\varphi_0\}$ has to be corrected in phase by multiplication with $\exp\{-i\,\varphi_0\}$
- The correction phase φ_0 consists of a frequency-dependent and a frequency-independent part
- The frequency-independent part can be adjusted by software before data acquisition via the receiver reference phase φ_{RX}
- The frequency dependent part is determined by the time the signal takes to pass through the spectrometer and by the receiver *deadtime* following an excitation pulse
- For optimum resolution the spectrum is needed in pure absorptive mode as $A(\Omega)$
- A frequency-dependent *phase correction* of the spectrum is a routine data processing step in high-resolution NMR spectroscopy

RF Excitation and Effective Field



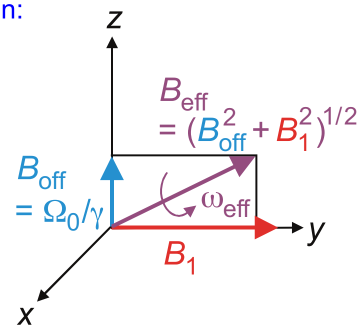
Non-selective excitation:
short pulse

Frequency distribution of the pulse excitation:
$B_1(\Omega) = B_1(0)\ \mathrm{sinc}\{\Omega t\}$
$= B_1(0)\ \sin\{\Omega t\} / (\Omega t)$



Selective excitation:
long sinc pulse

Frequency distribution of the pulse excitation $B_1(\Omega)$



Effective field in the rotating coordinate frame

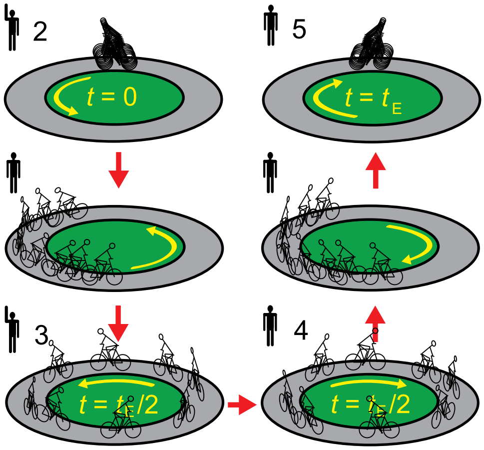
Frequency Distributions

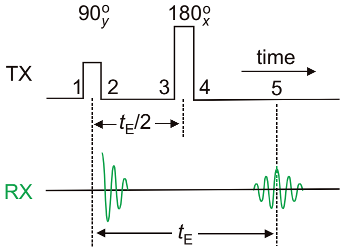
- The *rotating coordinate frame* RCF rotates with the rf frequency ω_{TX}
- Magnetization components M_i rotate in the RCF with frequencies $\Omega_{0i} = \omega_{0i} - \omega_{\mathrm{TX}}$
- To contact magnetization components in a range of frequencies Ω_{0i} with an *rf pulse* at frequency ω_{TX}, the pulse has to have a *frequency bandwidth*
- This frequency range is approximated by the inverse of the pulse width t_p
- A better measure for the bandwidth of the excitation is the *Fourier transform* of the excitation pulse
- For a rectangular pulse this is the *sinc* function with wiggles right and left
- Vice versa, the excitation can be made sharply frequency selective by excitation with an rf pulse having a sinc shape in the time domain
- This simple Fourier relationship is a convenient approximation valid only for flip angles smaller than 30°
- For a given component the offset frequency Ω_0 corresponds to a magnetic *off-set field* $B_{\mathrm{off}} = \Omega_0/\gamma$ along the z axis of the RCF
- The magnetization always rotates around the *effective field* $\boldsymbol{B}_{\mathrm{eff}}$, which is the vector sum of the offset field and the rf field with components Ω_0/γ and B_1
- The *rotation angle* around the effective field is given by $\gamma\, B_{\mathrm{eff}}\, t_p = \omega_{\mathrm{eff}}\, t_p$
- The rotation axis is close to the xy plane if $|B_1| >> |\Omega_0/\gamma|$
- If $|B_1| << |\Omega_0/\gamma|$, longitudinal magnetization cannot be rotated into the xy plane
- Low B_1 amplitudes are employed for frequency-selective excitation

Echoes

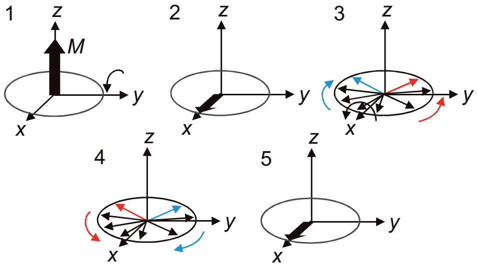
Erwin L. Hahn
(2005)
1921 - 2016

Racetrack echo

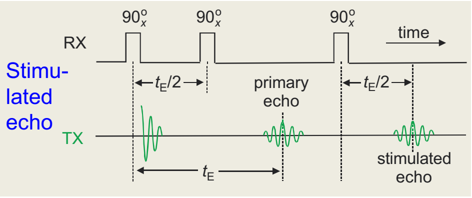




Hahn
echo



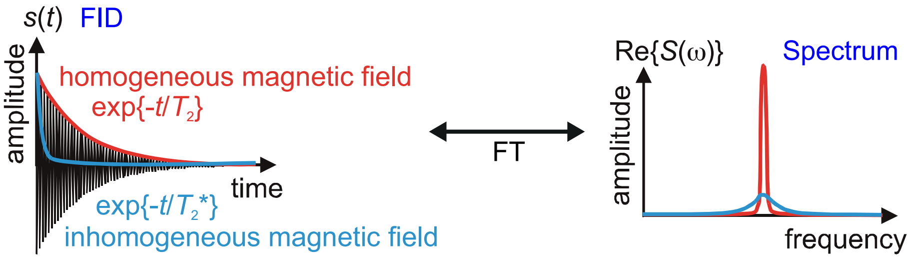
Stimu-
lated
echo



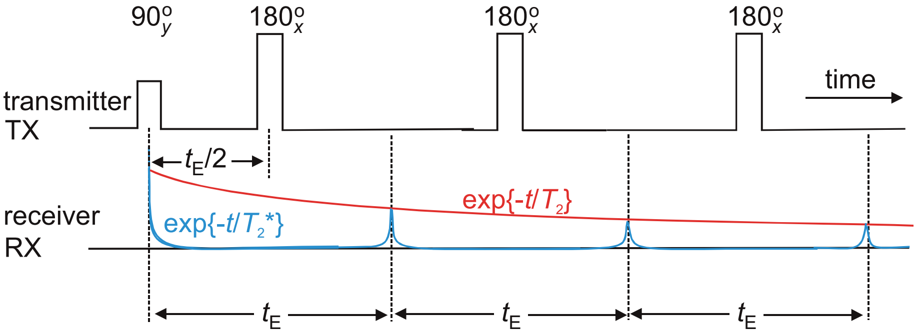
Relaxation

- *Relaxation* denotes the loss of *transverse magnetization* and build-up of *longitudinal magnetization*. The respective time constants are T_2 and T_1
- The loss of transverse magnetization due to different time-invariant local magnetic fields can stroboscopically be reversed by formation of *echoes*
- To generate a *racetrack echo* all bicyclists start at the same time but ride with different speeds. After a certain time all turn back and meet at the starting line forming the *echo* after twice that time
- Their total riding time is the *echo time* t_E
- The NMR *echo* has accidentally been discovered in 1949 by Erwin Hahn
- To form a *Hahn echo* all transverse magnetization components are rotated by 180° around an axis in the *xy* plane
- The direction of precession is maintained with this change of positions on the circle, and all magnetization components refocus at time t_E
- If some components randomly change their precession frequencies, the *echo amplitude* is irreversibly reduced
- Random frequency changes arise from fluctuating local magnetic fields associated with molecules in motion
- Transverse relaxation denotes the irreversible loss of the echo amplitude
- Both *relaxation times* T_1 and T_2 are determined by the type and time scale of molecular motion
- When splitting the 180° pulse of the Hahn-echo sequence into two 90° pulses separated by a time delay, one obtains the *stimulated echo* sequence

Echoes and Inhomogeneous Magnetic Fields



Multiple Hahn echoes following Carr, Purcell, Meiboom, and Gill (CPMG):



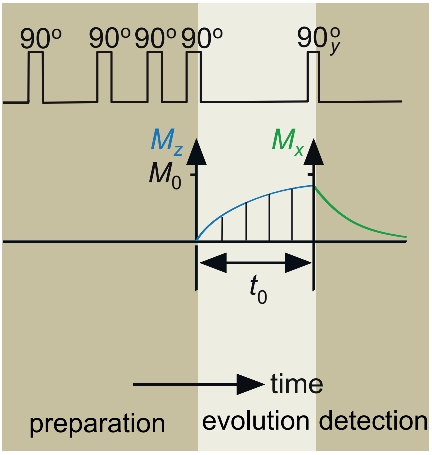
Multiple Echoes

- Transverse relaxation is often exponential with the time constant T_2
- In *inhomogeneous magnetic fields*, the FID decays faster with $T_2^* < T_2$
- The resonance signal in inhomogeneous magnetic fields is broad and small
- The envelope of the *FID* in homogeneous fields can be observed stroboscopically in inhomogeneous fields via the amplitude of many time-shifted echoes
- Instead of many *Hahn echoes* with different echo times t_E, the echo envelope can be observed by a single train of multiple Hahn echoes
- The rf pulse scheme for excitation of multiple Hahn echoes is the *CPMG sequence* named after their discoverers Carr, Purcell, Meiboom, and Gill
- The repetition times of $5T_1$ for regeneration of longitudinal magnetization between generation of different Hahn echoes are eliminated
- A waiting time of $5T_1$ is needed to regain about 99% of the *thermodynamic equilibrium magnetization*, because $\exp\{-5\} = 0.007$
- Besides the Hahn echo, stimulated echo, and CPMG echo train there are many other echoes and multiple-echo schemes to partially recover signal loss due to different nuclear spin interactions
- In the Hahn echo maximum, the inhomogeneity of the $\boldsymbol{B}_0$ field and the spread in chemical shifts do not affect the NMR signal

Pulse Sequences for Measurement of T_1

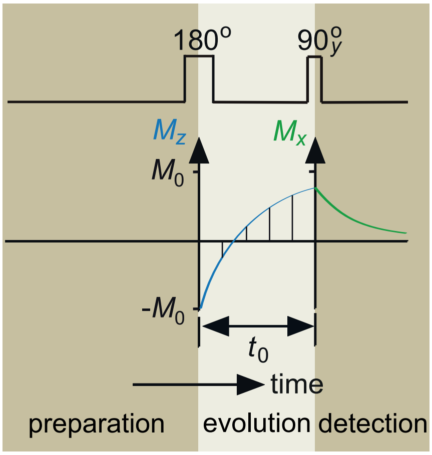
Saturation recovery:
$M_z(t_0) = M_0(1 - \exp\{-t_0/T_1\})$

Build-up of longitudinal magnetization following saturation



Inversion recovery:
$M_z(t_0) = M_0(1 - 2\exp\{-t_0/T_1\})$

Build-up of longitudinal magnetization following inversion

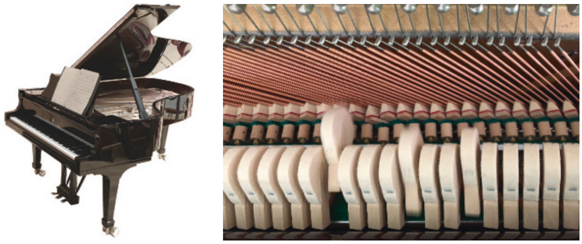


Determination of T_1

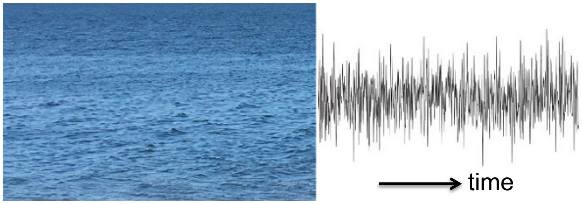
- *Longitudinal magnetization* cannot be directly observed
- Its momentary value can be interrogated via the amplitude of the FID following a 90° pulse
- There are two methods to measure the build-up of longitudinal magnetization, by *saturation recovery* and by *inversion recovery*
- For *saturation*, the spin system is irradiated with an aperiodic sequence of 90° pulses, which destroys all magnetization components
- For *inversion* of the longitudinal magnetization a 180° pulse is applied following the establishment of equilibrium magnetization after a waiting time of $5T_1$
- After such preparation of the initial magnetization a variable evolution time t_0 follows for partial recovery of the *thermodynamic equilibrium magnetization*
- After the waiting time t_0, the momentary value of the longitudinal magnetization is converted into the amplitude of the *transverse magnetization* by a 90° pulse
- The amplitude of the transverse magnetization is measured and evaluated for different values of t_0
- In homogeneous spin systems, the longitudinal relaxation follows an exponential law

Probing Resonance

Forced oscillation:
One resonance
probed at a time



Free oscillation:
Many resonances
probed at a time.
All initially in phase



Stochastic resonance:
Many resonances probed
at random and out of
phase

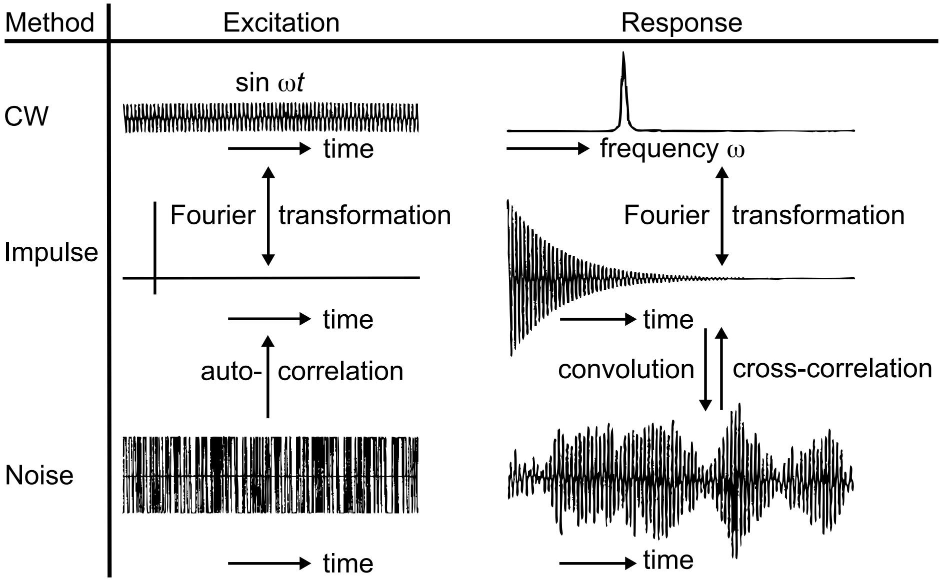
Methods for Measuring Resonances

- NMR is a *resonance phenomenon*. Consequently the basic NMR methods are the ones known from elementary physics to probe resonance phenomena
- There are three fundamental methods: forced oscillation, free oscillation and stochastic resonance
- *Forced oscillations* are known from wind instruments and string instruments like the violin, which are continuously agitated to produce the sound
- *Free oscillations* are known from string instruments like the piano or the guitar where strings are set into vibration with impulses
- *Stochastic resonance* is known from spectroscopy with the Michelson interferometer, where white noise randomly triggers vibrations, and the cross-correlation of excitation and response retrieves the impulse response
- The most versatile method of all is pulsed excitation. This already becomes clear when comparing sheet music for the piano and the violin

Pulse sequence for piano

Forced oscillations for violin

CW-, Fourier, and Stochastic NMR

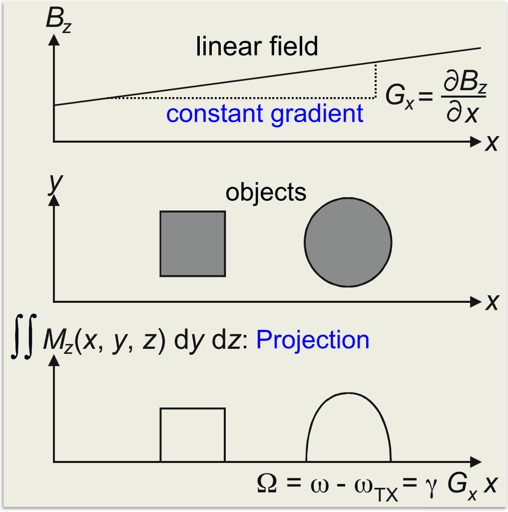


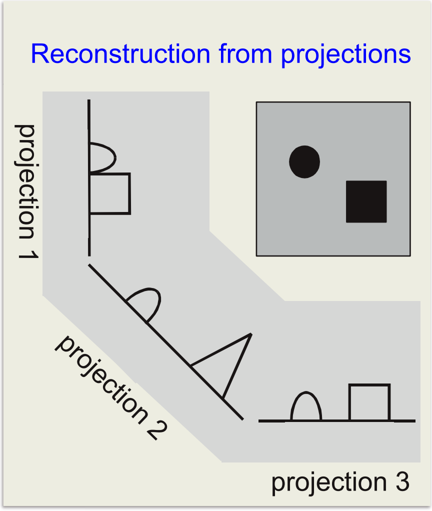
From B. Blümich, **Prog. Nucl. Magn. Reson. Spectr. 19** (1987) 331, Figs. 3, 5 with permission

Basic NMR Methods

- Probing resonance with *pulsed excitation* and measuring the impulse response or free oscillation is the state of the art when measuring NMR data
- With pulsed excitation, the acquired signal can be conditioned by manipulating the initial magnetization in preparation and evolution periods preceding the acquisition period
- Pulsed NMR is uniquely suited for extension to *multi-dimensional NMR*
- With short pulses large spectral widths can be excited, and many frequency components can be simultaneously measured (*multiplex advantage*)
- Measuring resonance by *forced oscillations* with *continuous waves* (CW) is slow, because the excitation frequency needs to be swept across the frequency range of the spectrum
- With *noise excitation* (stochastic NMR) large bandwidths are excited and can be measured simultaneously, but the experiment cannot readily be divided into different periods such as preparation, evolution, and detection periods
- The *excitation power* in CW NMR and stochastic NMR is several orders of magnitude lower than in pulsed NMR
- The different measuring methods are related via Fourier transformation, auto-, and cross-correlation of excitation and response

Space Encoding

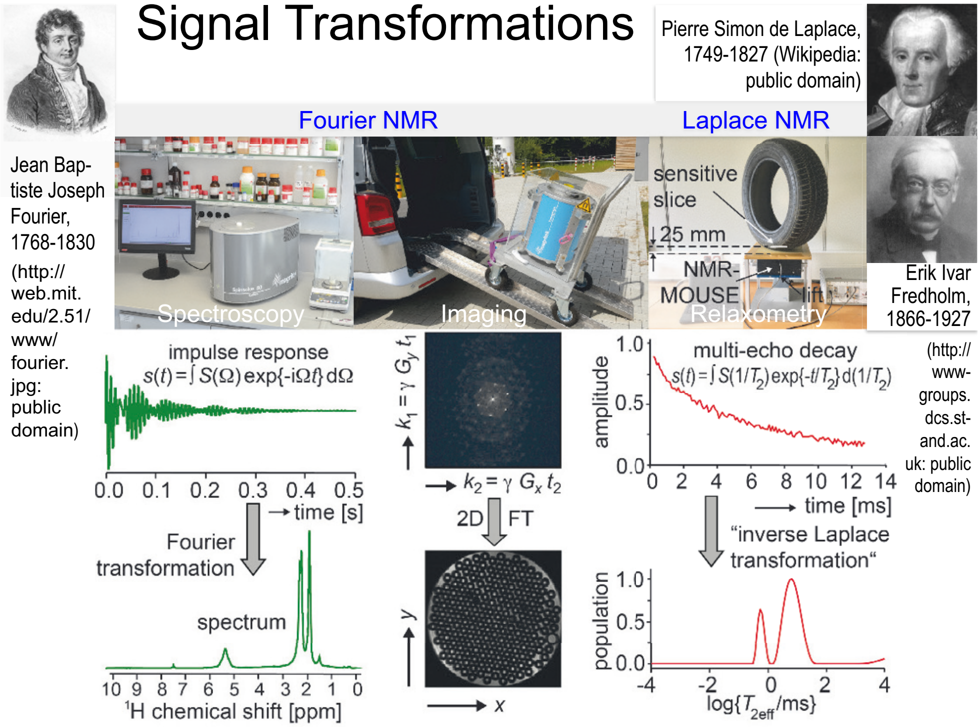




Magnetic Resonance Imaging (MRI)

- By exploring the proportionality of the resonance frequency ω_0 and the applied magnetic field B, signals from different positions in the sample can be discriminated if the magnetic field changes with position
- For a linear change of the magnetic field B_z with position, the magnetic field is characterized by a constant (space-invariant) *gradient G*
- In a linear field, the resonance frequency ω_0 is proportional to position, and the frequency axis of the NMR spectrum can be replaced by a space axis if the spectrum contains only one line
- The signal amplitude is determined by the number of nuclear spins at a particular position along the gradient direction
- This number is obtained by summation over all nuclei in the other two space directions
- Due to the large number of nuclei, the sum can be replaced by an integral over the magnetization density $M_z(x,y,z)$
- This integral is called a *projection*. It is a 1D image of the object
- $M_z(x,y,z)$ is also referred to as *spin density*
- From a set of projections acquired for different gradient directions an image of the object can be reconstructed in analogy to X-ray computed tomography
- The first magnetic resonance images were obtained in this way

Signal Transformations



Jean Baptiste Joseph Fourier, 1768-1830 (http://web.mit.edu/2.51/www/fourier.jpg: public domain)

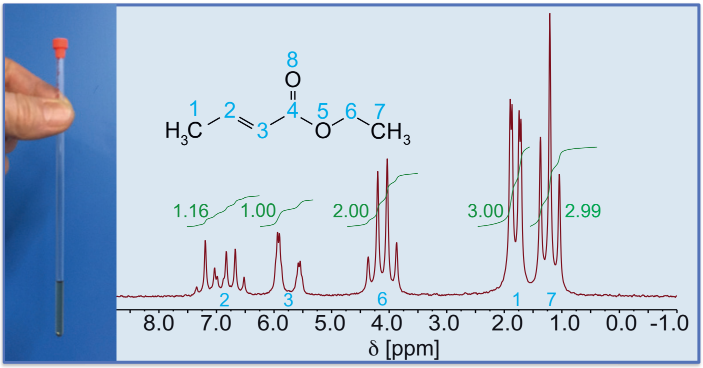
Pierre Simon de Laplace, 1749-1827 (Wikipedia: public domain)

Erik Ivar Fredholm, 1866-1927 (http://www-groups.dcs.st-and.ac.uk: public domain)

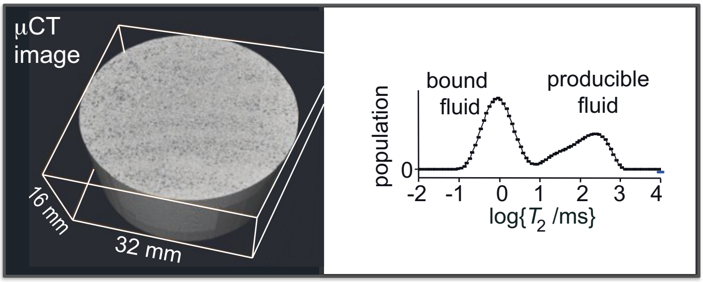
Fourier and Laplace NMR

- Bloch’s equation expresses the FID of a magnetization component in the rotating frame as the product of a real and a complex exponential function
  $$s(t) = M_{xy}(t) = M_{xy}(0)\exp\{-(1/T_2 + i\Omega_0)t\} = M_{xy}(0)\exp\{-(t/T_2\}\exp\{-i\Omega_0 t\}$$
- The *complex signal* $s(t)$ is Fourier transformed into a *spectrum* $S(\Omega)$ or an *image* revealing the *distribution of amplitudes* versus frequency or space
- The real exponential enters the linewidth in the spectrum or the spatial resolution in the image
- In inhomogeneous fields chemical shift differences cannot be observed (equivalent to $\Omega_0 = 0$), but the relaxation signal $s(n) = M_{xy}(0)\exp\{-(n\,t_E/T_2\}$ from the real exponential can be recalled in the maxima of a multi-echo train
- A relaxation signal $s(t)$ is inverted to a *distribution of relaxation rates* $S(1/T_2)$ by inverting a *Fredholm equation* of the first kind. In the NMR community this is somewhat generously referred to as *inverse Laplace transformation*
- The inversion algorithm assumes the relaxation signal to be a sum of real-valued exponential functions similar to the Fourier transformation, which takes the signal to be a sum of complex-valued exponential functions
- Forward and inverse Fourier transformations are stable operations even in the presence of noise, but Laplace inversion is not and needs to be stabilized
- *Fourier NMR* refers to the complex-valued exponential of the FID and *Laplace NMR* to the real-valued exponential

Analyzing Multi-Modal Distributions



43 MHz ^{1}H NMR spectrum of ethyl-crotonate. The relative multiplet integrals reveal the numbers of protons in each chemical group



T_2 distribution of water in travertine sandstone. The peak integrals are proportional to the amounts of bound and producible fluid

Component Analysis

- Most samples contain many magnetization components with different relaxation times T_{2i} and resonance frequencies Ω_{0i}, and their magnetization sum is measured in terms of the detected signal $s(t)$
$$s(t) = M_{xy}(t) = \Sigma_i M_{xyi}(0) \exp\{-(1/T_{2i} + i\Omega_{0i})t\}$$
- *Distributions of frequencies* Ω_{0i} (NMR spectra) and *distributions of relaxation rates* $1/T_{2i}$ with $\Omega_{0i} = 0$ are uniquely suited to quantify component fractions in terms of spin fractions $x_i = \int_{\Omega_1}^{\Omega_2} S(\Omega)\, d\Omega / s(0)$ and $x_i = \int_{(1/T_2)_1}^{(1/T_2)_2} S(1/T_2)\, d(1/T_2) / s(0)$ by integration of peaks in the distributions $S(\Omega)$ and $S(1/T_2)$ obtained by Fourier and inverse Laplace transformation of $s(t)$, respectively
- *Peak integrals* from *a high-resolution NMR spectrum* provide relative concentrations of chemical groups in a molecule or different molecules in a mixture
- *Peak integrals* from *distributions of relaxation times* provide relative concentrations of physical structures such as the fractions of amorphous and interfacial domains in *semi-crystalline polymers* and the relative amounts of *bound fluid* and *producible fluid* in porous medium
- If peaks or groups of peaks overlap, then two- and *multi-dimensional NMR* techniques may help to identify and separate the peaks belonging to different groups such as the *multiplets* in *J*-coupled ^{1}H spectra and the component spectra from mixtures
- For example 2D MRI separates a 1D projection into a 2D image